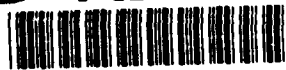


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Reaction of Methanol with Porous Silicon

by

John A. Glass Jr., Edward A. Wovchko and John T. Yates, Jr.

Submitted To

Surface Science

Surface Science Center
Department of Chemistry
University of Pittsburgh
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Reaction of Methanol with Porous Silicon

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Abstract

The reaction of both porous silicon and hydrogen covered (passivated) porous silicon with methanol was investigated. Adsorption of methanol onto porous silicon at 300 K resulted in cleavage of the O-H bond and formation of Si-OCH₃ and Si-H surface species. Heating of these surface species to ~500 K caused breakage of both the C-O and C-H bonds. This resulted in the formation of Si-H surface species and the incorporation of oxygen and carbon into the porous silicon layer. Attempts to adsorb methanol onto passivated porous silicon proved unsuccessful until removal of the Si-H surface species commenced at 600 K. In addition to oxygen and carbon incorporation, Si-OCH₃, Si-CH₃, and Si-H surface species were observed when excess CH₃OH (g) was used to drive the decomposition reaction. The stability of the Si-CH₃ species when excess CH₃OH (g) was present is likely due to oxygen and/or carbon passivation of the silicon surface.

I. Introduction

Silicon and silicon containing materials for electronic and optoelectronic device fabrication and catalytic silane and siloxane production form the basis for important technologies [1-6].

In producing silicon (100)-based devices [1,2] solvent cleaning and production procedures [7-10] and growth protocols [11-13] are employed. The effects of cleaning and production solvents on the silicon and on subsequently grown layers have not been widely studied. As silicon device fabrication techniques and requirements become more advanced and demanding, organic and aqueous solvents will be required to remove contaminants more efficiently. An important first step in moving toward these more advanced processes will be to determine the surface chemistry involved when these solvents interact with Si(100). Preliminary work has commenced with the investigation of H₂O. The primary focus has been to determine whether H₂O adsorbs by a dissociative or a nondissociative pathway and to determine the thermal decomposition properties of the resulting Si-H and Si-OH surface species[14-19]. The interaction of organic molecules, such as ethanol and methanol with Si(100), is less well studied [20-22]. Work by Crowell and co-workers [22] on ethanol decomposition on Si(100) appears to be one of the first few detailed studies to be completed for Si (100).

The possibility of basing the semiconductor industry on silicon alone by use of silicon based optoelectronic devices is financially appealing. However, the design and construction of light emitting silicon devices remains visionary. Porous silicon, which has shown promise in providing this elusive light emitting material, has been studied extensively with regard to its light emitting, photoluminescence, capability [23-30]. However, information is needed detailing the porous silicon surface chemistry with

organic solvents. Research into this surface chemistry is clearly warranted since the porous silicon used technologically will probably be subjected to cleaning procedures involving organic solvents.

The use of silicon to produce silanes and siloxanes, the Direct Synthesis, has been empirically optimized over many years [3, 4, 31]. Only very recently have studies focused on understanding specific modified catalysis involving copper and zinc mixed with silicon. An important benchmark in all of this work will be the determination of how reactants, such as methanol, interact with non-modified silicon.

These three examples illustrate that research into silicon reactivity with organic materials is an important area of research with benefits in a number of technologically important areas.

Method

Fourier Transform Infrared Spectroscopy (FTIR) used in the transmission mode can provide sensitive information concerning surface species and reactions. These transmission infrared studies may be extended to high reactant pressures not easily achievable using electron spectroscopy. However, in order for this technique to provide information, a large number of surface sites must be available. This limits the types of materials that can be studied to high surface area materials where the number of surface sites exceeds $\sim 10^{18}$ atoms / cm². The Si(100) surface without modification, with only 6.8×10^{14} atoms / cm², could therefore not provide the surface site density needed for transmission infrared measurements.

Porous silicon, first produced in the 1950's by Uhlir [32] and Turner [33], has been shown to be a high surface area (180-225 m²/cm³) network of channels (20 Å to 100 Å wide) with crystalline and amorphous regions [34, 35]. Such surfaces make excellent substrates for obtaining transmission FTIR spectra from surface species adsorbed on

silicon. Issues raised concerning the use of porous silicon to represent Si(100) have been previously addressed by a number of researchers [18, 35, 36]. Both George and Smith showed that little significant difference is observed between porous silicon and Si(100) reactivity [18, 35, 36].

Therefore, we have begun to study, by FTIR, the standard organic solvents used in semiconductor cleaning and processing and in the Direct Reaction synthesis of siloxanes by using porous silicon, produced from Si(100). This paper details the adsorption and reaction of CH₃OH with porous silicon.

II. Experimental

Porous Silicon Preparation

Si(100) single crystals (Virginia Limited) used in this study were 1.3 cm x 1.3 cm x 1.5 mm p-type B doped (5-10 Ω cm) crystals. Slots, 1.3 mm deep, were cut into each edge using a string saw. Each crystal following cutting was cleaned, using and the RCA technique, and stored under de-ionized water [7-9]. The etching apparatus, shown in Figure 1, consisted of a Si(100) crystal, a thin tantalum plate and a copper lead compressed between two pieces of a Teflon holder and secured with six Teflon screws. The opening in the bottom Teflon piece and the Viton o-rings allowed 0.75 cm² of the Si(100) crystal to be exposed to the homogeneously mixed solution containing 275 ml of 48% HF (aq) and 75 mL of anhydrous CH₃CH₂OH. Nitrogen was bubbled into the solution for ~ 1hr. to de-oxygenate the solution. Following the nitrogen purge, the 2 μ m porous silicon layer was produced by a current of 100 mA for 20 seconds (133 mA / cm²). The crystal with the porous layer was then removed from the etching apparatus and dipped into 48% HF (aq) for 15 seconds to remove any native surface oxide and any

residual contamination from the solution. Finally, the crystal was dried and stored, typically less than 1 hr., in a clean environment until mounting into the infrared cell.

Crystal Mounting

All experiments were conducted in a special infrared cell shown in Figure 2 [37]. The cell consisted of a stainless steel cube with six-conflat flanges connected to a Thermonics rotary seal. This seal permits rotation through 360°, allowing orientation of the sample relative to the infrared beam (See lower part of Figure 2). In addition, sample rotation avoids SiO deposition on the KBr windows during heating. Inserted into this rotary seal is a reentrant Dewar containing a 34 mm dia. power-thermocouple feedthrough connection at the bottom. In each experiment a porous silicon crystal was securely mounted by placing two pieces of tantalum foil into the slots previously cut into the crystal and connecting them to the feedthrough power leads. In addition, a Chromel / Alumel, type K, thermocouple wrapped in tantalum foil was inserted into the top slot and connected to the feedthrough for temperature control. Controlled heating using feedback from the thermocouple was achieved electronically with a Honeywell UDC 500 digit temperature controller and a custom built 0-50A, 0-100V power supply. Cooling of the sample was provided by either N₂(l) or a combination of N₂(l) and ethanol. With the cooling from the Dewar and the electronically controlled heating, the temperature of the sample could be maintained to within ±2 K in the range of 300 K to 900 K. The lower section of the cell consisted of, in addition to the rotary seal holding the sample, two KBr optical windows with mechanically pumped double Viton o-ring seals, a quartz window, and a gas/vacuum line connection. All pumping and gas delivery were handled from the gas/vacuum connection. The system was pumped with a N₂(l) cooled zeolite sorption pump, a 50 L/s Balzers turbomolecular pump, and a Varian 20 L/s ion pump. Base pressures in this combined system were typically <1 × 10⁻⁸ Torr after 20 hours of

evacuation. In addition to the pumps, the vacuum system contained a UTI Model 100C quadrupole mass spectrometer for leak checking and two capacitance manometers (0-10 Torr and 0-1000 Torr) for accurate pressure measurements.

Infrared Measurements

All infrared spectra were recorded using a nitrogen purged Mattson Research Series I Fourier transform infrared spectrometer. Data were processed and manipulated using Mattson Fourier Infrared Software Tools (FIRST). The spectrometer was equipped with a liquid nitrogen cooled HgCdTe detector and was capable of obtaining spectra from 5000 - 500 cm^{-1} . In this study spectra were measured by averaging 1024 scans at a spectral resolution of 2 cm^{-1} . All spectra were recorded at 300 K under evacuation. Single beam spectra from the KBr windows were measured by rotating the porous silicon sample out of the beam (See Off Beam in Figure 2). Absorbance spectra were obtained by ratioing single beam spectra of the sample with the window single beam spectra.

Materials, Exposures, and Annealings

Anhydrous CH_3OH (Baker 99.95%), and isotopically labeled CH_3OD (Merck, 99 % isotopic purity), CD_3OH (Merck, 99 % isotopic purity), and $^{13}\text{CH}_3\text{OH}$ (Cambridge Isotopes, 99% isotopic purity) used in this study were transferred to pre-evacuated and baked glass bulbs and five freeze-pump-thaw cycles were performed on each prior to use. The gas/vacuum line was pre-treated with one, 2 Torr, 30 second cycle of the desired methanol adsorbate and then evacuated. All exposures to methanol were made at a pressure of 9 Torr. Surface hydrogen removal from the electrochemically prepared porous silicon was completed by flash annealing, in vacuum, to 750 K prior to methanol exposure. This porous silicon was then exposed to methanol and heated from 300 K to

900 K in vacuum for study of the thermal behavior of the surface species. Studies involving the hydrogenated porous silicon were carried out by heating the porous silicon from 300 K to 900 K in methanol vapor at 9 Torr pressure.

III. Results and Discussion

Electrochemical Etching and Removal of Hydrogen from Porous Silicon

The FTIR spectra of porous silicon after electrochemical etching and after removal of surface Si-H has been detailed previously [36, 38]. Figure 3 shows the FTIR results we obtained before electrochemical etching (A), after electrochemical etching (B), and after the final flash annealing (C) procedures. Figure 3A (bottom spectrum) shows the Si-Si lattice modes for the crystal in the range of 1600 cm^{-1} to 700 cm^{-1} . These bands correspond to the infrared lattice absorption bands reported in the literature [39]. The FTIR difference spectrum after electrochemical etching for 20 sec at 100 mA is presented in Figure 3B (middle spectrum). The $\nu(\text{Si-H}_x)$, $\nu_{\text{sc}}(\text{Si-H}_2)$, $\delta(\text{Si-H})$, and $\delta(\text{Si-H}_2)$ modes can be clearly seen at $2140\text{--}2089\text{ cm}^{-1}$, 913 cm^{-1} , 667 cm^{-1} , and 630 cm^{-1} respectively. Interestingly, the $\nu(\text{Si-H}_x)$ region of the spectra is clearly resolved into three distinct bands at 2140 cm^{-1} , 2113 cm^{-1} , and 2089 cm^{-1} . Assignment of these bands has been a topic of much debate [40]. We assign them based on thermal properties as $\nu(\text{Si-H}_3)$ (2140 cm^{-1}), $\nu(\text{Si-H})$ (2113 cm^{-1}), and $\nu(\text{Si-H}_2)$ (2089 cm^{-1}) in agreement with literature assignments [36, 38]. Finally, after heating to 750 K, difference spectrum C was obtained (top spectrum). All of the silicon hydride spectral features are gone and only a small absorbance due to $\nu(\text{Si-O-Si})$ and $\delta(\text{Si-OH})$ is seen at 976 cm^{-1} and 861 cm^{-1} . Presumably these two bands result from the decomposition of adsorbed water originating from the cell walls upon heating the silicon sample to 750 K.

Reaction of Unpassivated Porous Silicon with CH₃OH and CH₃OD

Following removal of hydrides from the porous silicon surface, 9 Torr of CH₃OH was allowed to react at 300 K. The resulting spectrum, Figure 4A, shows the chemisorption of CH₃OH on porous silicon. The spectrum indicates that the adsorption proceeds by cleavage of the O-H bond to form Si-CH₃O and Si-H on the surface. This result is fully consistent with the behavior of CH₃OH on Si(111) [41, 42] and with other molecules containing O-H bonds when adsorbed on porous silicon [18, 19] and Si(100). The individual spectral features are listed in Table 1. Confirmation of the cleavage of the OH bond in this dissociative process was carried out by adsorption of an identical amount of CH₃OD onto a second porous silicon sample. This spectrum is shown in Figure 4B and is identical to the spectrum from CH₃OH adsorption in all respects except for production of a ν (Si-D) mode at 1521 cm⁻¹. Spectral features for CH₃OD are also given in Table 1. Interestingly, in the CH₃OH adsorption spectrum the Si-H frequency shifts downward from the 2113 cm⁻¹ absorbance produced by the electrochemical etch. This change is due either to interactions taking place between the adjacent OCH₃ and the H on the surface or to new types of surface sites which develop after flash annealing of the sample. Both the lack of intensity at 913 cm⁻¹ and the shift to lower wavenumber eliminates the possibility of Si-H₂ surface species formation from CH₃OH, or that oxygen impurities within the porous layer are affecting the Si-H frequency [18].

Thermal Annealing of Si-OCH₃ and Si-H Surface Species

Heating of the Si-OCH₃ and Si-H covered porous silicon surface, Figures 5, 6, and 7, resulted in further surface decomposition effects. The ν (CH₃) modes (centered at 2946 cm⁻¹), the δ (CH₃) mode (1461 cm⁻¹), the ρ (CH₃) mode (1182 cm⁻¹), and the ν (C-O) mode (1086 cm⁻¹), Figure 5(A) and Figure 6, all decrease uniformly to zero with

only slight changes in frequency over the temperature range 500 K to 700 K. This argues that the OCH_3 surface species on porous silicon is stable only up to ~ 500 K. This is consistent with data derived from EELS and IRAS studies on $\text{Si}(100)$ in which the OCH_3 surface species began to decompose at 500 K [21]. The initial ν (Si-H) mode (2091 cm^{-1}) decreases in intensity starting at ~ 550 K, Figure 5(B), in accordance with other studies [36] of hydrogen on porous silicon. This is accompanied by intensity increases corresponding to new Si-H species at 2269 cm^{-1} and 2169 cm^{-1} (spectra not shown). These new Si-H species are stable to much higher temperatures than the 2091 cm^{-1} species, as represented by the 2269 cm^{-1} intensity behavior in Figure 5(B). These modes are interpreted as being due to Si-H species in which the silicon atom is bound to the surface via oxygen atoms [18, 19, 43]. We designate the modes at 2269 cm^{-1} and 2169 cm^{-1} as ν ($\text{O}_x\text{Si-H}$) modes and note that they begin to develop at approximately the same temperature that the CH_3 modes and the C-O modes from the OCH_3 species begin to decrease in intensity. In addition to the changes that occur in the Si-H region, the low frequency region of the spectrum also shows dramatic changes upon heating the surface. New modes observed at 998 cm^{-1} , 775 cm^{-1} and 761 cm^{-1} are assigned as ν (Si-O-Si), δ ($\text{O}_x\text{Si-H}$), and ν (Si-C) respectively. These assignments are based on previous studies of porous silicon [18, 19, 43] and our isotopic labeling studies with $^{13}\text{CH}_3\text{OH}$ and CD_3OH . Here the lack of shift in the 775 cm^{-1} mode upon carbon-13 labeling and the loss of intensity upon deuterium labeling indicated that the 775 cm^{-1} band corresponds to a Si-H mode. In addition, the 761 cm^{-1} band is identified as a ν ($\text{Si-}^{12}\text{C}$) mode based on its shift to 740 cm^{-1} when carbon-13 is employed (Table I). Intensity variations versus annealing temperature, Figure 6, clearly show that the intensity of both ν (Si-O-Si) and δ ($\text{O}_x\text{Si-H}$) begins to increase at about 500 K, where the CH_3 modes, the C-O mode, and the ν (Si-H) mode (2091 cm^{-1}) begin to lose intensity. The slightly later development of the ν (Si-O-Si) intensity is probably due to the inability to accurately measure the intensity because of the large ν (C-O) and ν (Si-O-Si) spectral overlap. The ν (Si-C) mode at

761 cm^{-1} begins to show increased intensity only above 650 K. This latent development of the Si-C band at 761 cm^{-1} is counter to the initial decomposition temperature for the OCH_3 species. Interference from δ ($\text{O}_x\text{Si-H}$) (775 cm^{-1}) and incomplete lattice mode subtraction may play a role in this inability to record the ν (Si-C) signal near 450-600 K. Finally, after heating at 900 K, a difference spectrum, Figure 7, records that all the OCH_3 and H surface species have been removed and only the final decomposition products, yielding the ν (Si-O-Si) and ν (Si-C) modes, are evident.

This information concerning the thermal behavior of Si- OCH_3 and Si-H on porous silicon yields a picture of the OCH_3 and H surface species decomposition. At low temperatures (< 500 K) both OCH_3 - and H-surface species are stable. In the range of 500 K to 700 K the OCH_3 moiety decomposes by breakage of the C-H and C-O bonds in the OCH_3 to form an oxygen- and carbon-covered surface. This is supported by the loss of intensity of the CH_3 modes and of the ν (C-O) mode, and the concomitant intensity gain of the ν (Si-O-Si) mode. Further evidence for the formation of Si-O-Si linkages at 450-500 K (as opposed to 550 K as observed) is given by the shifts observed in the ν (Si-H) frequency (from 2091 cm^{-1} to 2169 cm^{-1} and 2269 cm^{-1}) and the δ (Si-H) frequency (from 667 cm^{-1} to 775 cm^{-1}) at 500 K. These spectral shifts are indicative of oxygen being bonded to silicon that contains chemisorbed hydrogen. Presumably the carbon is also incorporated into the silicon even though no immediate indication of the Si-C signal is observed. In addition, the Si-H (2091 cm^{-1}) surface species is removed in the temperature range 550-700 K, as has been previously demonstrated on porous silicon [36]. At temperatures above 700 K, only the shifted ν (Si-H) modes, the ν (Si-O-Si) mode, and the ν (Si-C) mode are observed. All other intensities are obscured or virtually zero.

Confirmation of C-H bond breakage

In order to confirm the C-H bond breakage and creation of Si-H surface species from the decomposition of the CH₃ group of the OCH₃, CD₃OH was studied between 300 K and 900 K under identical conditions as the CH₃OH. If no C-H breakage were to occur no Si-D signal should be observed. However, Figure 8 clearly shows an increase in the Si-D signal at the same temperature (~450-500 K) where C-H intensity loss was observed for CH₃OH (Figure 5). Therefore, cleavage of both the C-O and C-H bonds is occurring above ~450 K in the decomposition of OCH₃ on porous silicon. In addition to confirming the decomposition of Si-OCH₃ some of the Si-D signal shifts to higher frequency (1647 cm⁻¹). This shift in Si-D frequency to higher values is due to oxygen incorporation in the silicon surface, as was seen for the Si-H species.

Reaction of Passivated Porous Silicon with CH₃OH

The reaction between the passivated porous silicon layer and methanol, Figure 9, significantly differed from the reaction of the unpassivated sample. The initial reaction of the methanol with the porous layer to form OCH₃ and H surface species did not begin to occur until ~600 K. Spectroscopic observations at various temperatures indicates that desorption of hydrogen from the passivating layer at temperatures ≥ 600 K generates open sites for methanol reaction. Since this 600 K transition point is ~100-150 K above the decomposition temperature of the OCH₃ species on hydrogen-free silicon, the spectra show the formation of the thermal decomposition products seen previously [this work, 18, 19, 43]. These results are in agreement with other studies which have shown that a hydride layer on silicon surfaces provides a protective barrier for surface reactions [44, 45, 46]. Two important spectral differences were observed for methanol decomposition on

silicon surfaces compared to these heating experiments in methanol vapor involving hydrogen-passivated silicon. First, a new spectral feature located at 1276 cm^{-1} is observed as soon as the methanol begins to react. This previously unseen feature is indicative of a $\delta(\text{CH}_3)$ mode from CH_3 directly bound to silicon [43, 47, 48]. Unfortunately, the $\nu(\text{CH}_3)$ modes from Si-CH_3 species are not resolvable due to the $\nu(\text{CH}_3)$ from Si-OCH_3 species. Secondly, the frequencies of the $\nu(\text{Si-O-Si})$ and the $\nu(\text{Si-C})$ modes from the OCH_3 decomposition are shifted to higher values when gas phase methanol is present during the heating (Table II). These shifts are consistent with the oxygenation of the surface from the large amount of methanol being decomposed on the surface. Reaction of the silicon surface with $\text{CH}_3\text{OH(g)}$ therefore results in two new observations compared to studies of OCH_3 decomposition. First, the formation of a Si-CH_3 species occurs; this species exhibits a high degree of thermal stability (above 900 K) compared to CH_3 adsorbed on Si(100) (decomposes at 600 K) [48]. This stabilization of Si-CH_3 likely stems from the extensive oxygen and/or carbon incorporation. Second, the vibrational frequency of the Si-C surface species is influenced by incorporated oxygen as was observed for Si-H_x surface species.

Figure 10 shows the relationship between the intensities and annealing temperatures for the CH_3OH decomposition on the passivated sample. Clearly, no reaction occurs until approximately 600 K. At 600 K, and above, spectral features rapidly develop for the $\nu(\text{Si-O-Si})$ and $\nu(\text{Si-C})$ modes, the decomposition products of OCH_3 . The $\nu(\text{Si-CH}_3)$ mode, and the oxygenated Si-H mode ($\nu(\text{Si-H})$ at 2255 cm^{-1}) also develop above 600 K. In addition, the $\nu(\text{Si-H})$ mode from the original passivated layer rapidly decreases in intensity over the same temperature range.

IV. Conclusions

The following features for CH_3OH decomposition on porous silicon have been observed:

1. Methanol reacts with unpassivated porous silicon to form Si-OCH_3 and Si-H surface species by breakage of the O-H bond at 300 K.
2. Heating these surface species results in the decomposition of the Si-OCH_3 at > 450 K by bond breakage of both the C-H bond and the C-O bonds to form Si-H surface species and to incorporate oxygen ($\nu(\text{Si-O-Si})$) and carbon ($\nu(\text{Si-C})$) into the porous silicon.
3. Further heating beyond 600 K results in loss of the Si-H surface species by the loss of hydrogen gas as has been reported previously [36].
4. Reaction of methanol vapor with hydrogen-passivated porous silicon results in no reaction until 600 K.
5. Temperatures > 600 K cause methanol vapor to react with the freshly formed open sites. The Si-OCH_3 , Si-CH_3 , and Si-H surface species and incorporated oxygen (Si-O-Si) and carbon (Si-C) are formed.
6. Further thermal treatment of the Si-OCH_3 , Si-CH_3 , and Si-H surface under CH_3OH (g) removes the remaining Si-H surface species and generates more intense Si-O-Si , Si-C , and Si-CH_3 spectral features.
7. The stabilization of a Si-CH_3 species during reaction with excess CH_3OH is likely due to the oxygen and/or carbon passivation of the silicon surface due to the high surface coverage of these species derived from the CH_3OH .

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Figure Captions:

- Figure 1:** Electrochemical apparatus used to produce a 2 μm porous layer on Si(100) crystals.
- Figure 2:** Infrared cell used to measure transmission infrared spectra on porous silicon samples.
- Figure 3:** (A) FTIR spectra of silicon crystal before any modification; (B) after formation of porous silicon layer (difference); and (C) after removal of surface hydrides produced in the formation of porous layer (difference).
- Figure 4:** FTIR spectra of porous silicon after removal of hydrogens and adsorption of 9 Torr of (A) CH_3OH ; and (B) CH_3OD .
- Figure 5:** Infrared absorbances of $\nu(\text{CH}_3)$, $\delta(\text{CH}_3)$, $\rho(\text{CH}_3)$, $\nu(\text{Si-H})$, and $\nu(\text{Si-H})$ at 2946 cm^{-1} , 1461 cm^{-1} , 1182 cm^{-1} , 2091 cm^{-1} and 2269 cm^{-1} respectively as a function of annealing temperature for CH_3OH adsorbed on unpassivated porous silicon.
- Figure 6:** Infrared absorbances of $\nu(\text{C-O})$, $\nu(\text{Si-O-Si})$, $\nu(\text{Si-C})$ and $\delta(\text{O}_x\text{Si-H})$ at 1086 cm^{-1} , 998 cm^{-1} , 761 cm^{-1} and 775 cm^{-1} respectively as a function of annealing temperature for CH_3OH adsorbed on unpassivated porous silicon.
- Figure 7:** FTIR difference spectra detailing the loss of Si-OCH_3 and Si-H intensity and the gain of Si-O-Si and Si-C intensity from the adsorption and thermal annealing of CH_3OH adsorbed on porous silicon.
- Figure 8:** Infrared absorbances of $\nu(\text{Si-D})$ and $\nu(\text{Si-D})$ at 1527 cm^{-1} and 1647 cm^{-1} as a function of annealing temperature for CD_3OH adsorbed on unpassivated porous silicon.

Figure 9: FTIR spectra showing the reaction of 9 Torr of CH_3OH with passivated porous silicon as a function of temperature.

Figure 10: Infrared absorbances of $\nu(\text{CH}_3)$, $\nu(\text{Si-CH}_3)$, $\nu(\text{Si-H})$, $\nu(\text{Si-O-Si})$, $\nu(\text{Si-C})$ and $\nu(\text{Si-H})$ at 2954 cm^{-1} , 1276 cm^{-1} , 2255 cm^{-1} , 1033 cm^{-1} , 815 cm^{-1} and 2111 cm^{-1} respectively as a function of annealing temperature for the reaction of 9 Torr of CH_3OH with passivated porous silicon.

Table I: Infrared Assignments for Adsorption of CH₃OH, CH₃OD, and ¹³CH₃OH on Porous Silicon.

<u>CH₃OH</u> (cm-1)	<u>CH₃OD</u> (cm-1)	<u>¹³CH₃OH</u> (cm-1)	<u>Assignment</u>	<u>Reference</u>
2971	2973	2964	ν (CH ₃)	this work, 42
2946	2946	2939	Modes ^a	
2844	2844	2839		
2838	2838	2834		
2269 ^b	2267 ^b	2267 ^b	ν (O _x Si-H)	18, 36, 43
2169 ^b	2171 ^b	2172 ^b	Modes	
2091	-	2090	ν (Si-H) Mode	
-	1648 ^b	-	ν (O _x Si-D) Mode	
-	1521	-	ν (Si-D) Mode	this work, 18, 36
1461	1462	1457	δ (CH ₃)	this work, 42
1447	1448	1441	Modes ^a	
1182	1183	1173	ρ (CH ₃) Mode ^a	this work, 21, 42
1086	1084	1069	ν (C-O) Mode ^a	this work, 21, 42
998 ^b	998 ^b	998 ^b	ν (Si-O-Si) Mode ^b	this work, 43
775 ^b	774 ^b	770 ^b	δ (O _x Si-H) Mode ^b	18, 36
761 ^b	763 ^b	740 ^b	ν (Si-C) Mode ^b	this work, 49

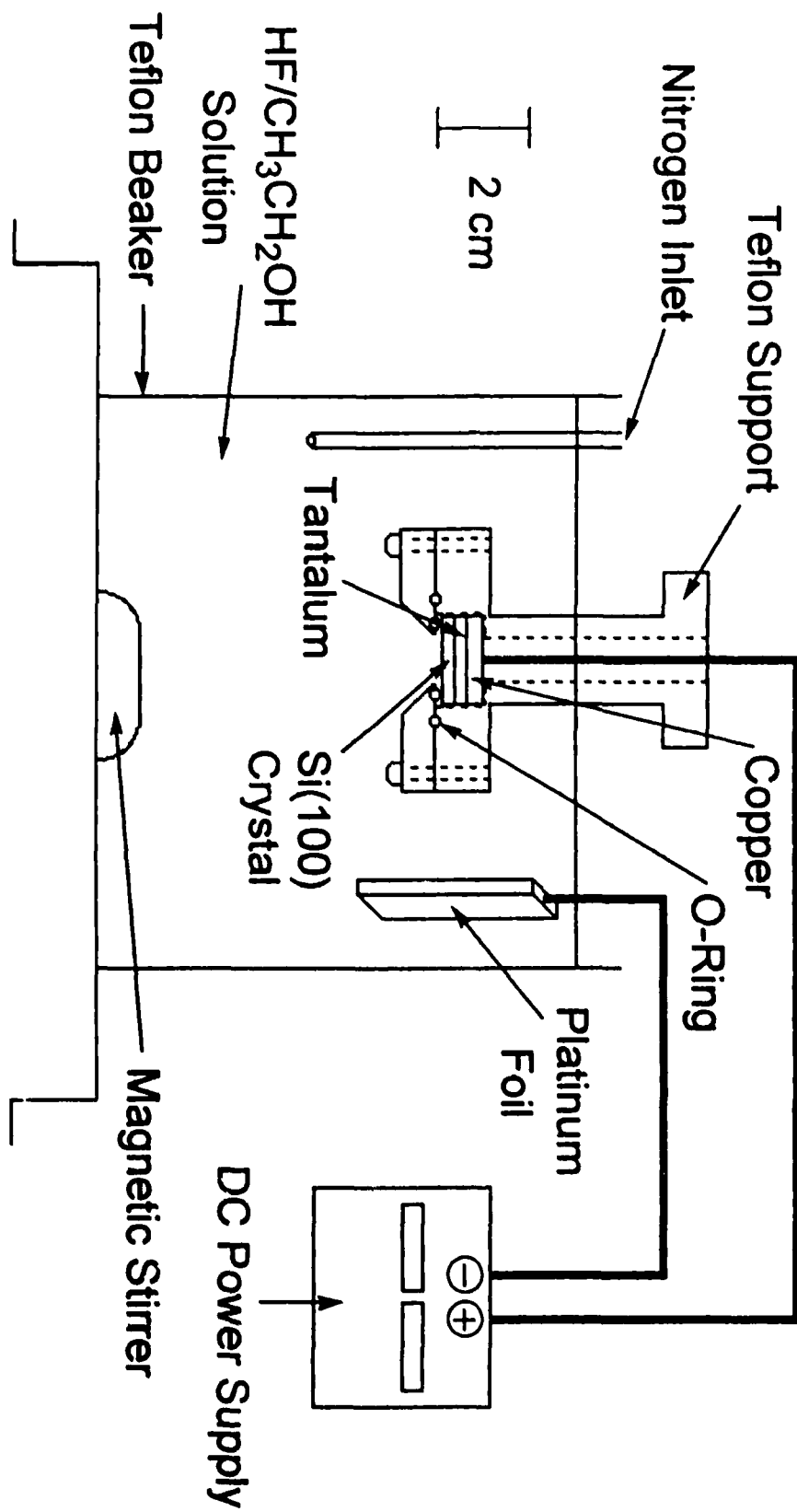
a -- Modes from OCH₃ species.

b -- These infrared absorbances occur after the porous silicon sample is annealed to 700 K.

Table II: Shifts in ν (Si-O-Si) and ν (Si-C) Frequency upon Extensive Reaction with Methanol Vapor.

Mode	Frequency without excess methanol. (cm ⁻¹)	Frequency with excess methanol. (cm ⁻¹)
ν (Si-O-Si)	998	1025
ν (Si-C)	761	815

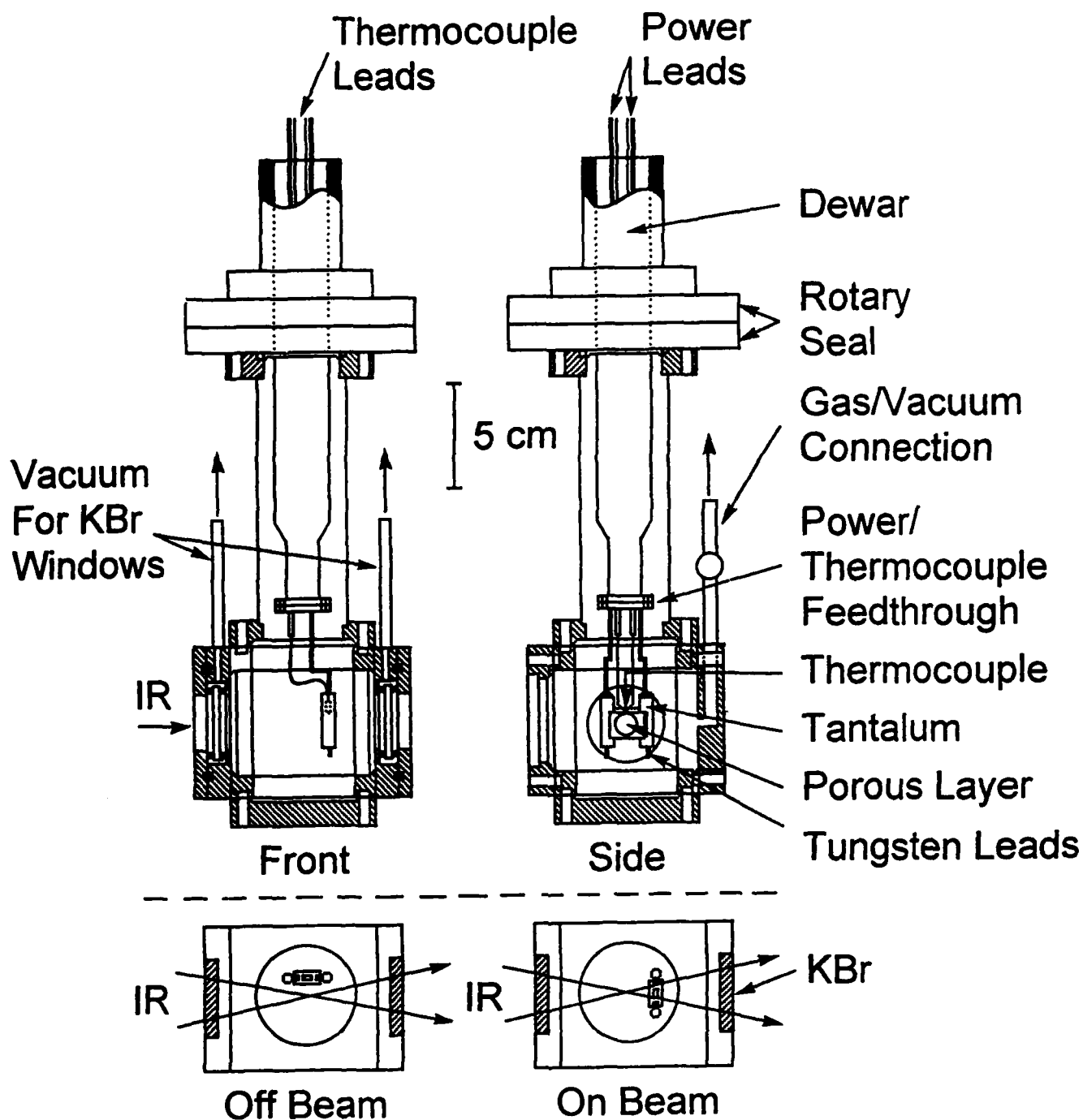
Porous Silicon Etching Apparatus



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Figure 1

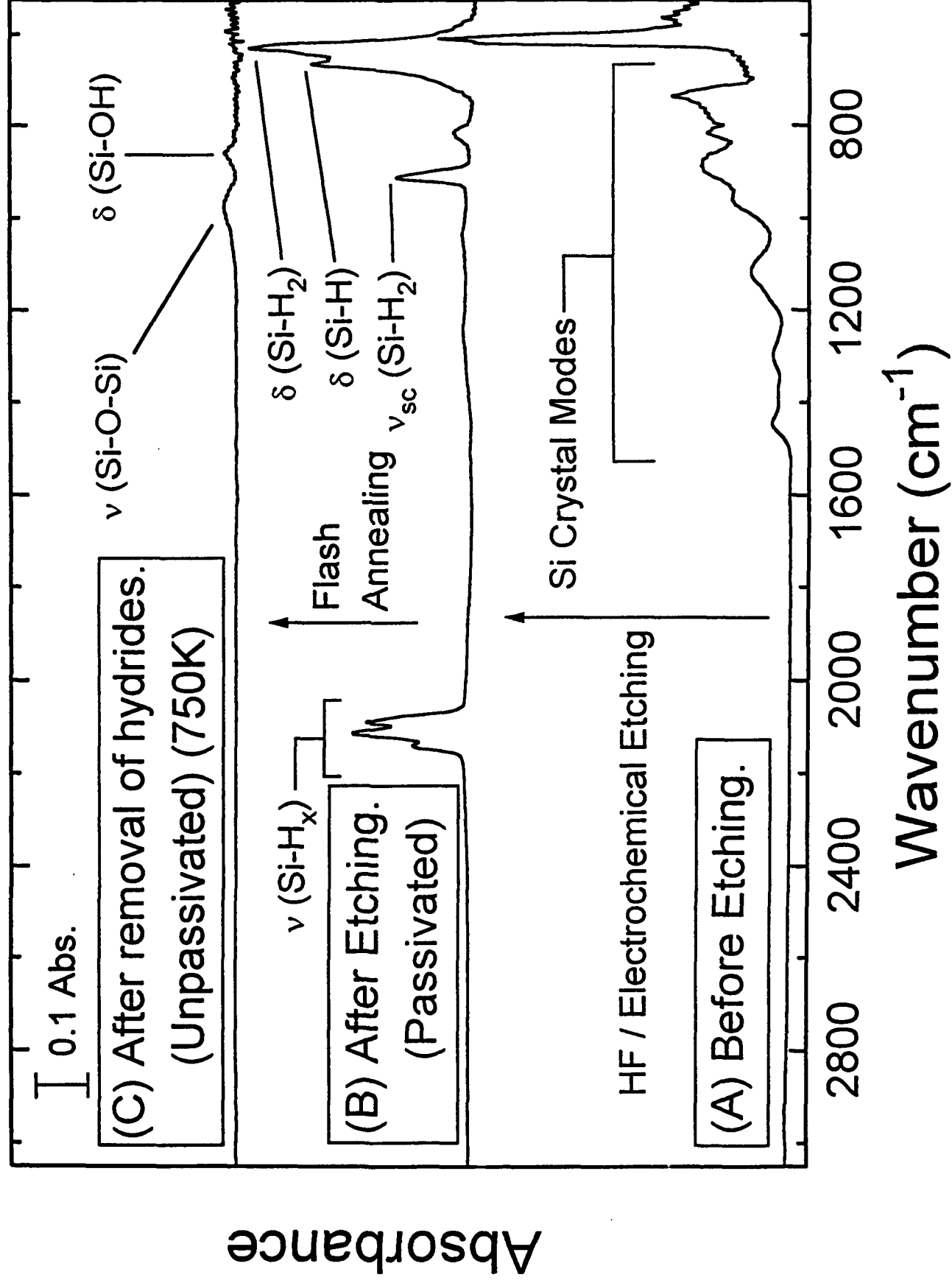
Infrared Cell



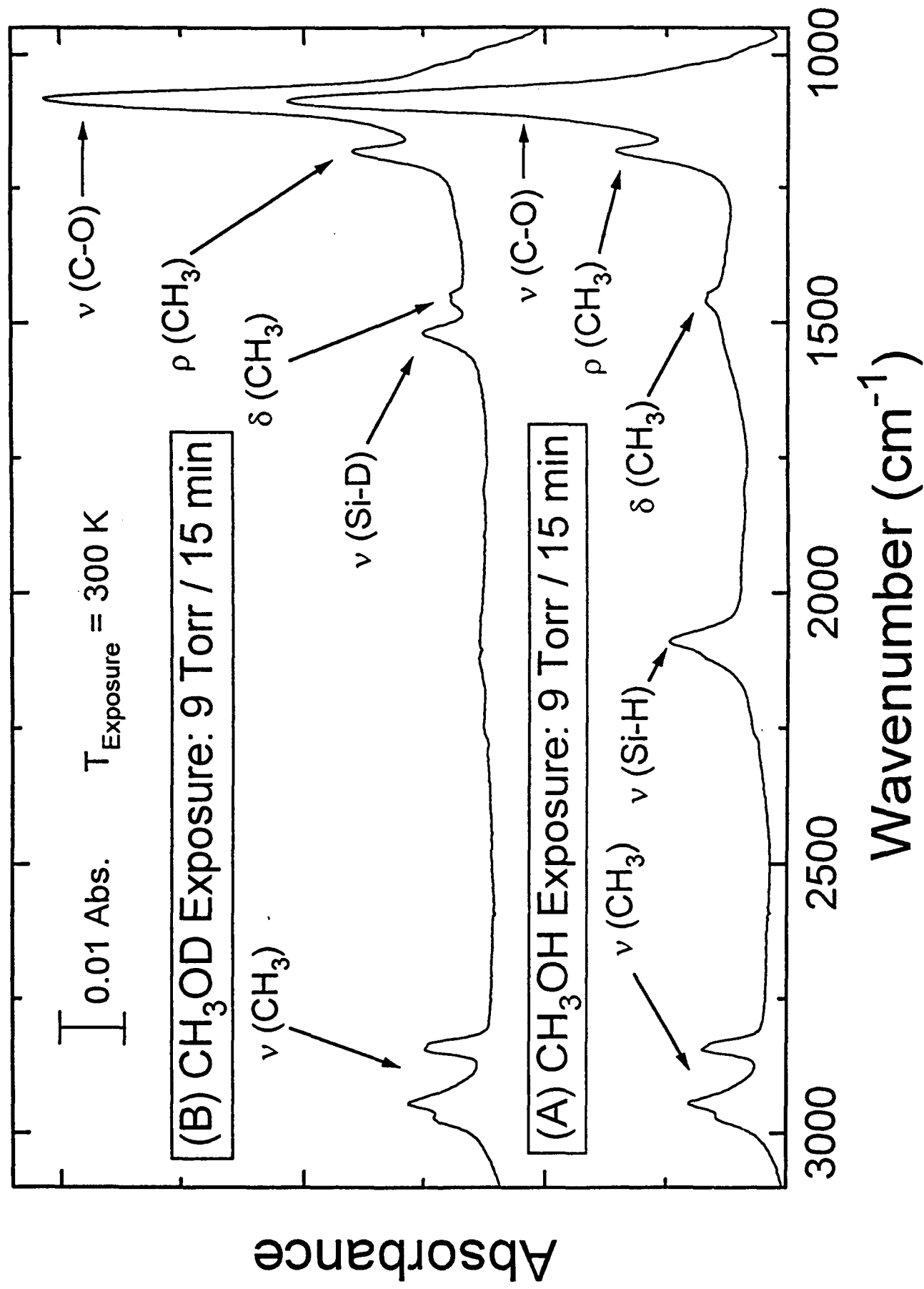
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Figure 2

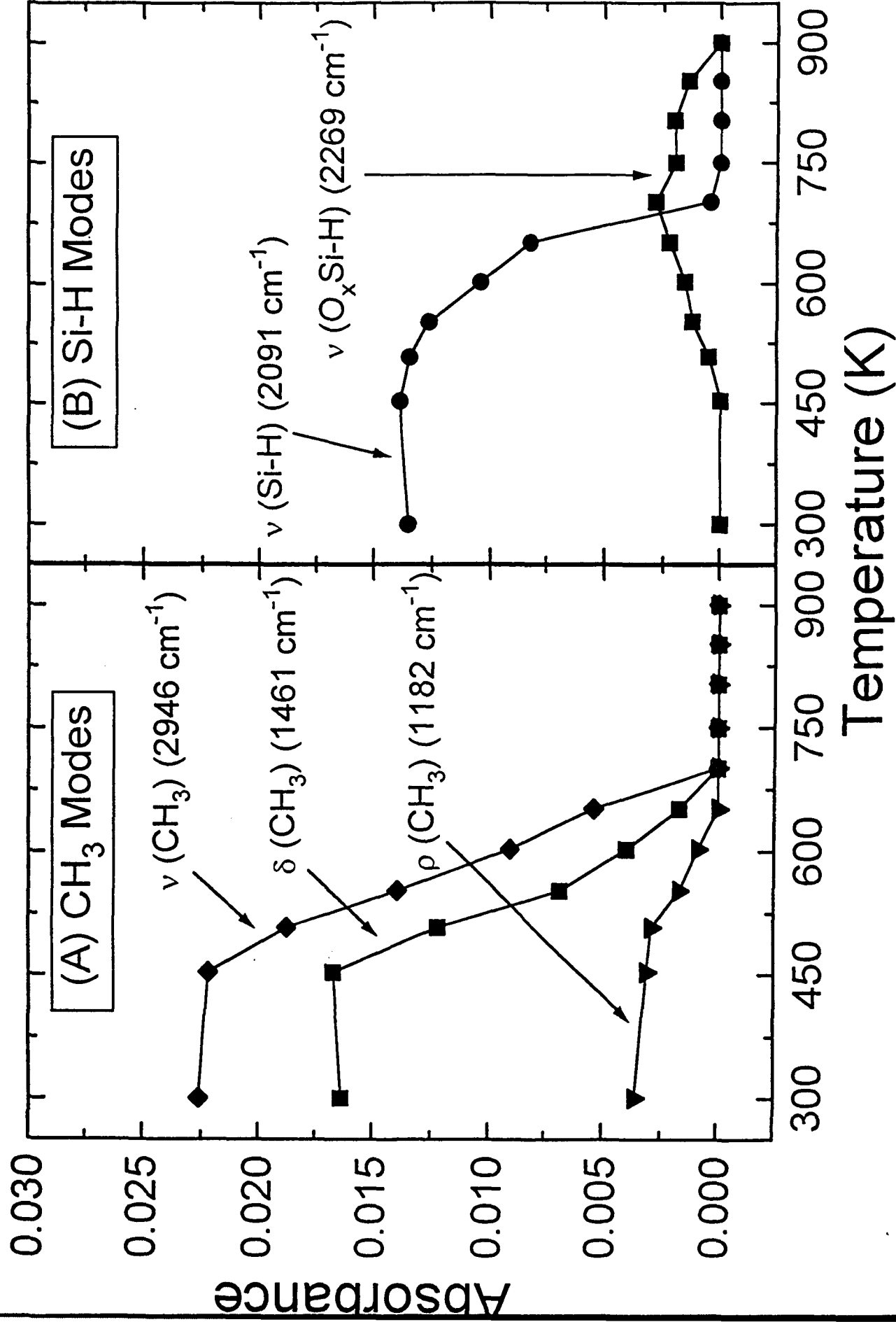
Formation of Passivated and Unpassivated Porous Silicon.

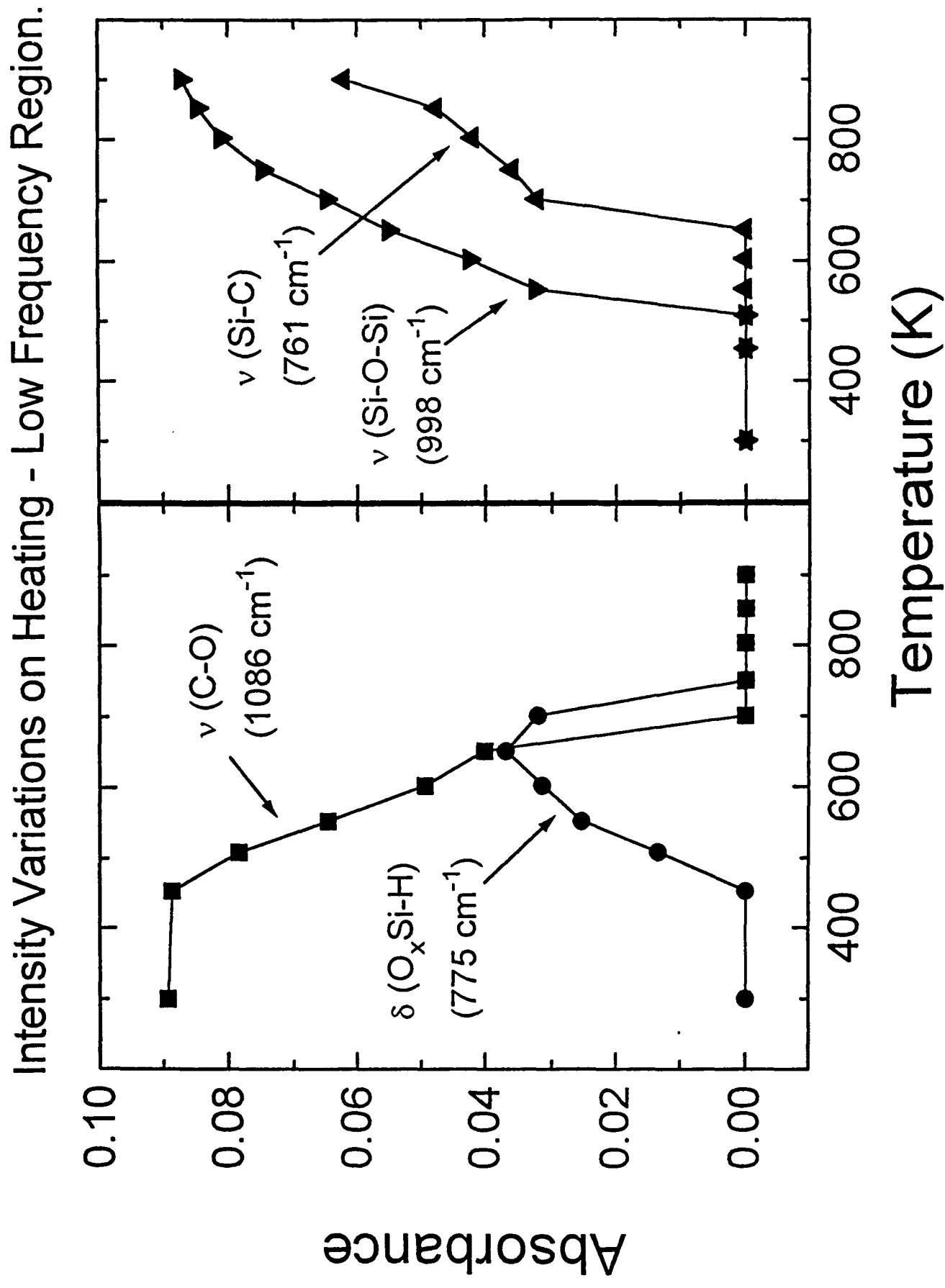


Methanol Adsorption on Unpassivated Porous Silicon.

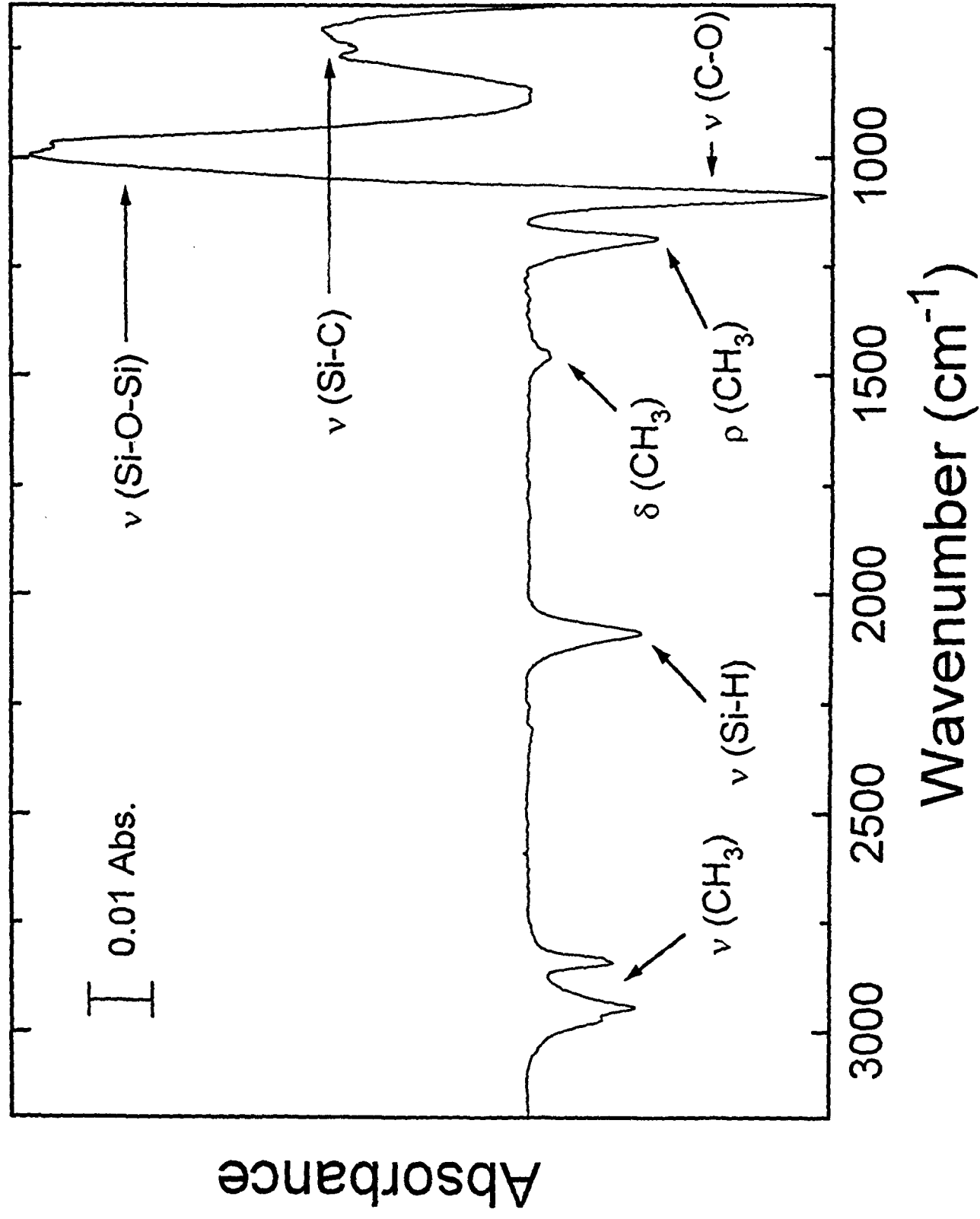


Intensity Variations on Heating - High Frequency Region.

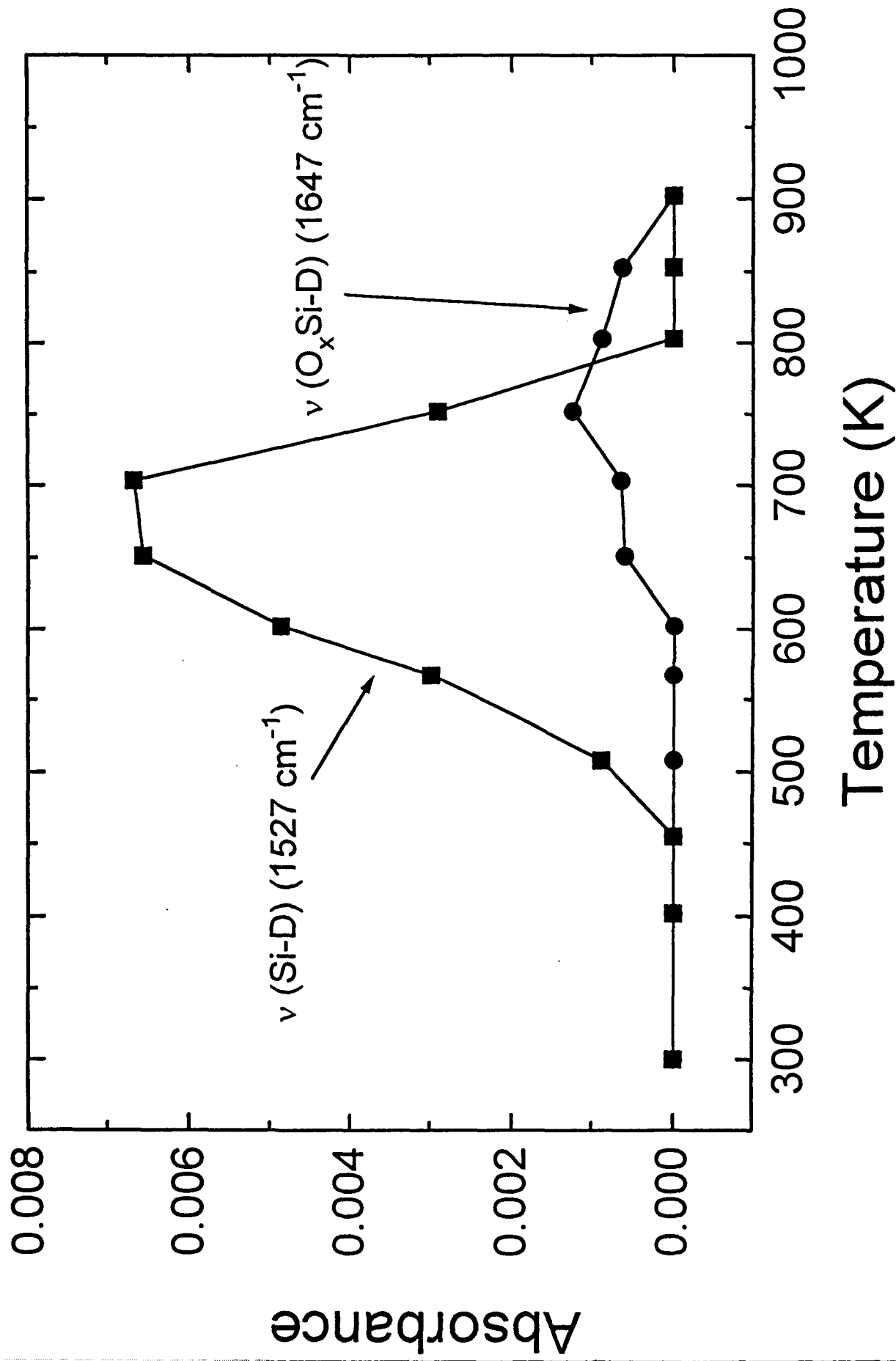




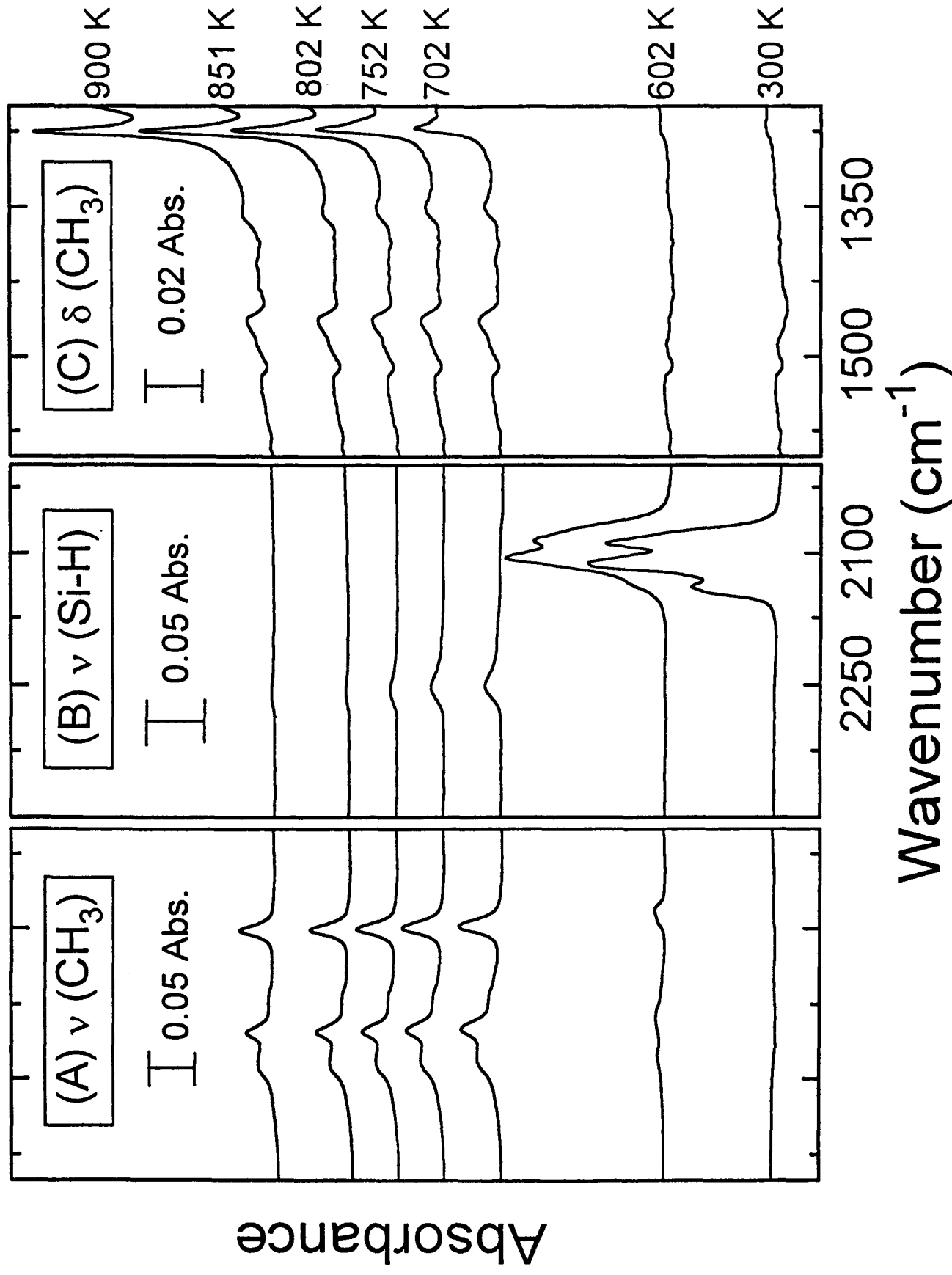
Difference Spectra after Annealing CH_3OH Covered Si to 900 K.



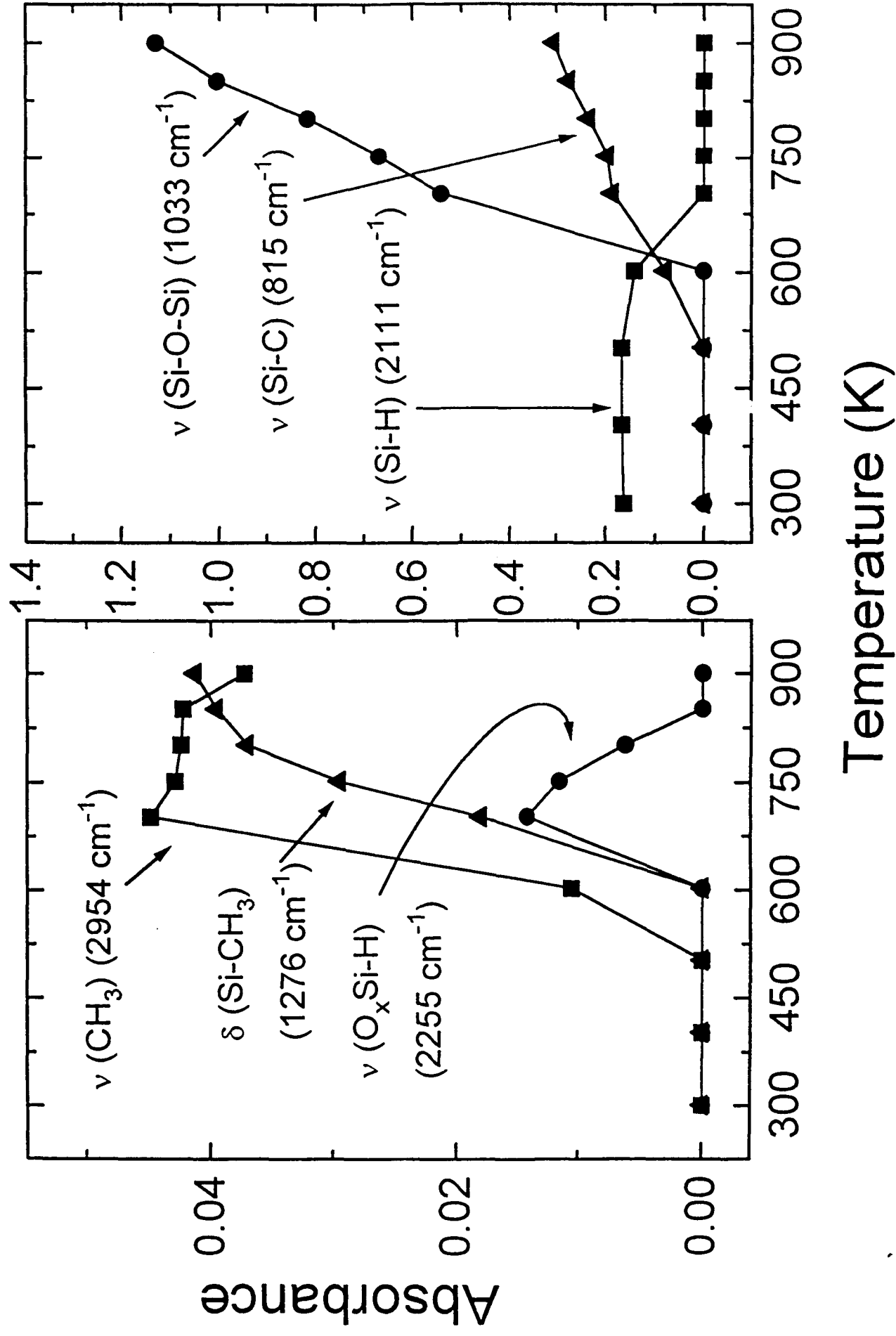
Intensity Variations on Heating - CD_3OH on Porous Silicon.



Thermal Reaction of Passivated Porous Silicon with $\text{CH}_3\text{OH(g)}$.



Intensity Variations on Heating Passivated Silicon in $\text{CH}_3\text{OH(g)}$.



Enclosure # 3

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